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Ultimate performance of polymer:fullerene bulk heterojunction tandem solar cells

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We present the model calculations to explore the potential of polymer:fullerene tandem solar cells. As an approach we use a combined optical and electrical device model, where the absorption profiles are used as starting point for the numerical current-voltage calculations. With this model a maximum power efficiency of 11.7% for single cells has been achieved as a reference. For tandem structures with a ZnO/poly(3,4-ethylenedioxythiophene)/poly(styrenesulphonic acid) middle electrode an ultimate efficiency of 14.1% has been calculated. In the optimum configuration the subcell with the narrowest band gap is placed closest to the incoming light. Consequently, tandem structures are expected to enhance the performance of optimized single cells by about 20%. © *2011 American Institute of Physics*. [doi:10.1063/1.3549693]

In the past two decades, interest in organic solar cells was boosted by the discovery of photoinduced very fast electron transfer from conjugated polymers to fullerenes,[1] leading to the development of bilayer solar cells using these materials as active layers.[2] Blending of the electron-accepting and electron-donating material in a nanoscopic bulk heterojunction significantly increased the performance of solar cells based on polymer donors and fullerene acceptors.[3] The efficiency of organic polymer:fullerene bulk heterojunction solar cells has been steadily increasing in the past decade, going from 2.5% efficiency in 2001[4] to 3.5% in 2003,[5] up to 5.5% in 2007,[6,7] and recently an efficiency of 7.4% has been reported.[8] The performance improvement mainly originated from the development of low band gap polymers, of which the absorbance has an enhanced overlap with the solar spectrum. In the past years, theoretical studies have been undertaken to understand what the fundamental performance limits are for organic bulk heterojunction solar cells.[9,10] These studies predict a practical power conversion efficiency limit of about 10%–11% for single cells. The efficiency calculations done by Koster *et al.*[10] employed an electrical model including field and temperature dependent dissociation of bound electron-hole pairs as well as space-charge formation in the case of unbalanced charge transport.[11] The model was based on the assumption that the optical profile can be taken as constant and that the photocurrent is directly dependent on the total amount of absorbed photon flux. In a later stage we extended this model to a combined optical and electrical model.[12] The combined optical and electrical calculations confirmed that the exact shape of the absorption profile in the solar cells is not very critical as long as the active layer thickness (ALT) does not exceed 250 nm.[12] As a result the estimation of a maximum efficiency of 11% for a single cell, done with a constant profile, is expected to be approximately correct. For organic tandem solar cells an estimation of the maximum efficiency was presented by Dennler *et al.*[13] Their calculations are mainly based on optical considerations. For the electrical part a number of assumptions were used; for example, the fill factor (FF) of the subcells was assumed to be 0.65, the external quantum efficiency was fixed at 65%, the current of the tandem cell was taken equal to current of the subcell with the lowest current, and it was assumed that the FF of the tandem was identical to the FF of the subcells. An electrical device model for tandem solar cells was recently developed by Hadipour *et al.*[14] It was demonstrated how the *J-V* characteristics of a tandem cell can be constructed from the characteristics of the two subcells. In case of an unequal current generation the middle electrode is charged, thereby enhancing the electric field and photocurrent of the current limiting cell. As a result the current of the tandem solar cell is higher than the current of the limiting cell. This effect was also demonstrated experimentally by Gilot *et al.*[15] In order to accurately estimate the ultimate efficiency of organic tandem solar cells a combined optical and electrical approach is required. In this study, we extended the combined optical and electrical model from single cells to tandem cells. We demonstrate that a single organic solar cell has a maximum power conversion efficiency (η_{max}) of 11.7%, whereas for a tandem cell a maximum efficiency $\eta_{max}=14.1\%$ is calculated. As a result with tandem cells an efficiency increase of about 20% can be realized as compared to a fully optimized single cell.

As a first step toward the calculation of the maximum efficiency of a tandem cell we first reevaluate the efficiency calculations on single cells. We start with modeling of the optical properties of a typical single junction solar cell stack. As a substrate a 0.75 mm thick silica is taken with, on top of it, a 130 nm thick layer of indium tin oxide (ITO) as transparent front contact, a 40 nm thick layer of poly(3,4ethylenedioxythiophene)/poly(styrenesulphonic acid) (PEDOT:PSS) as transparent anode, a layer of a polymer:fullerene blend with variable thickness as active layer, and 1 nm of evaporated lithium fluoride (LiF) and 100 nm of evaporated aluminum (Al) as cathode. The optical properties of Al were taken from literature[16] and those of silica, ITO, PEDOT:PSS, and LiF were determined by variable angle ellipsometry using a Woollam variable-angle spectroscopic ellipsometer (VASE). The optical parameters of the polymer:fullerene blend are proposed to be an admixture of those of

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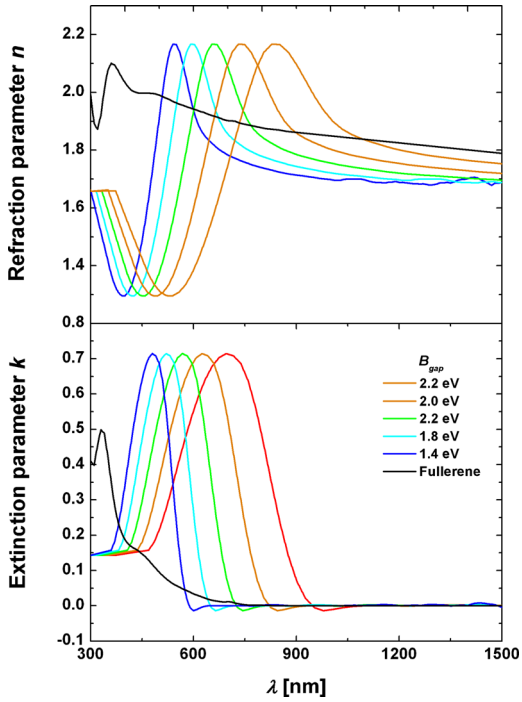

FIG. 1. (Color online) Complex refractive parameters of the polymer for five different B_{gap} and of the fullerene as a function of wavelength λ. Note that the polymer parameters are redshifted for B_{gap} lower than 2.2 eV.

the polymer and those of the fullerene added in a 2:1 ratio, which is their volumetric ratio instead of their mass ratio, which is 1:1. The optical properties of the fullerene part are taken to be those of methanofullerene [6,6]-phenyl C61-butyric acid methyl ester (PCBM) as reported by Hoppe *et al.*[17] Those of the polymer part are based on the properties of MDMO-PPV, as have been determined by variable angle ellipsometry using a Woollam VASE ellipsometer, but in the calculations the band gap B_{gap} is varied. The optical parameters of the polymer as a function of B_{gap}, together with those of PCBM, are shown in Fig. 1. As can be seen in Fig. 1, B_{gap} is varied between 1.4 and 2.2 eV in steps of 0.1 eV. The complex refractive parameters of the polymer with $B_{gap}=2.2$ eV are those of MDMO-PPV, while those having a lower B_{gap} are redshifted by an amount of energy equal to the 2.2 eV minus B_{gap}. We take the electronic energy levels of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the fullerene and polymer to be 3.8 and 6.1 eV (PCBM) and 3.5 and 4.9–5.7 eV (polymer) varied in steps of 0.1 eV, respectively. The difference of 0.3 eV between the polymer and fullerene LUMO levels is the assumed minimum necessary energy difference required for efficient electron transfer.[11] As a result of this reduction of 0.3 eV the energy gap between the LUMO of the fullerene and the HOMO of the polymer varies between 1.1 and 1.9 eV in steps of 0.1 eV in our calculations. With a typical loss of 0.4 eV from the energy gap to the open circuit voltage (V_{oc}) the resulting V_{oc} varies from 0.7 to 1.5 eV in steps of 0.1 eV. The electrical parameters of the active layers used in the electronic device model are temperature $T=295$ K, relative dielectric constant $\varepsilon_r=3.4$, electron and hole mobilities $\mu_{n,p}=10^{-7}$ m^2/V s, which is an optimum value,[18] charge pair separation $a=1.8$ nm, and decay rate of the bound e-h pair $k_f=2\times10^4$ s^{-1}, which are similar to the parameters obtained for slowly dried P3HT:PCBM cells.[19] An equal mobility for electrons and holes avoids efficiency losses due to too slow or unbalanced charge transport with resulting space-charge formation.

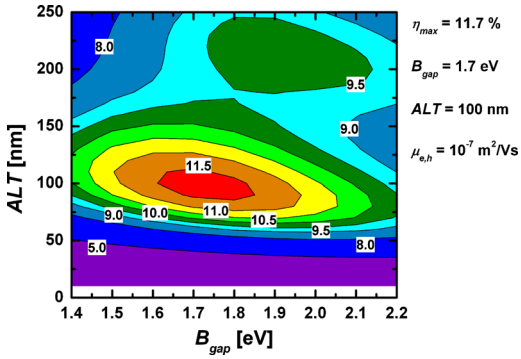

FIG. 2. (Color online) Power conversion efficiency η as a function of polymer band gap B_{gap} and ALT. Note that the submaximum has a higher B_{gap} because of the larger ALT.

Using these parameters a single cell is simulated as a reference, with its ALT being varied between 10 and 250 nm with a step size of 10 nm and B_{gap} being varied between 1.4 and 2.2 eV with a step size of 0.1 eV. In Fig. 2 the power conversion efficiency (η) is shown as a function of B_{gap} and ALT. Clearly visible is the maximum efficiency $\eta_{max}=11.7\%$ for $B_{gap}=1.7$ eV and ALT=100 nm, where $V_{oc}=1.00$ V, the short-circuit current (J_{sc}) is 156.5 A/m^2, and the FF is 74.3%. There is also a second efficiency maximum of 9.9% for $B_{gap}=1.9$ eV and ALT=220 nm. The η_{max} is similar in magnitude to η_{max} found by Liang *et al.*,[8] where the optical absorption profile was taken as a constant. In the calculations presented here also the optical absorption profiles are taken into account, but since the relevant sample thicknesses do not exceed 250 nm the results are very similar. The two main factors that determine η_{max} are the absorbed photon flux and B_{gap}. With regard to B_{gap}, it is clear that narrower band gaps will increase the overlap with the solar spectrum, such that more photons are being absorbed and thus η increases. On the other hand, a smaller B_{gap} also limits the V_{oc} of the cell. The resulting η_{max} is the best compromise, with the ALT such that the absorbance is in an interference maximum of the incoming photon flux.

The tandem cell structure is similar to that of the single cell but has an additional middle electrode and a second active layer between the first active layer and the cathode. As middle electrode a 30 nm thick layer of zinc oxide (ZnO) is taken in combination with a 40 nm thick layer of neutralized PEDOT:PSS.[20,21] This layer serves as the transparent anode of the second active layer consisting also of a polymer-:fullerene blend. The layer thickness of the two active layers is varied between 10 and 250 nm in steps of 10 nm. The tandem cells are electrically connected in series. Hadipour *et al.*[14] developed a generalized methodology, which obtains the current-voltage characteristic of organic tandem solar cells by knowing the electrical performance of both subcells. Here, we use this methodology to calculate the performance of the tandem cells. The ALT and B_{gap} of each cell are varied individually like in the single cell scenario, resulting in $25\times25\times9\times9\approx50.000$ different tandem cell variations. In Fig. 3 the optical absorption profile is shown for an optimized tandem cell. The front cell has a band gap B_{gap}^{front} and the back cell has a band gap B_{gap}^{back}, where the front cell is the subcell nearest to the glass substrate and the back cell is the subcell nearest to the Al cathode. The layer thicknesses of

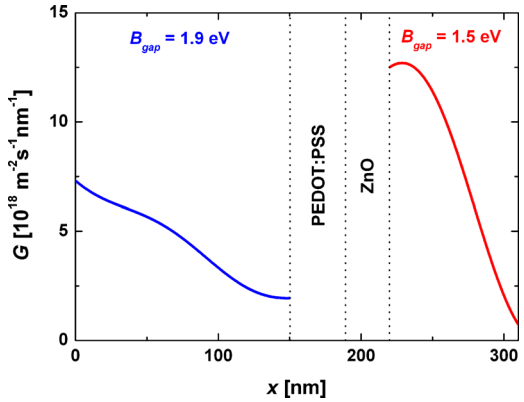

FIG. 3. (Color online) Calculated exciton generation rate profiles plotted vs the position x in an optimized tandem solar cell. Note that G is the rate of generated excitons per square meter per second per nanometer thickness of an active layer.

the front active layer [front layer thickness (FLT)] and back active layer [back layer thickness (BLT)] amount to FLT =150 nm and BLT=90 nm, respectively. For these layer thicknesses the interference pattern is such that the absorption for both cells is maximized at these band gaps.

Due to the four variables that determine the performance (B_{gap}^{front}, B_{gap}^{back}, FLT, and BLT) and that only two of them can be simultaneously displayed in a plot, we show η as a function of the front cell band gap (B_{gap}^{front}) and the back cell band gap (B_{gap}^{back}) in Fig. 4. Note that each value of η for a pair of band gap values is the highest one for all FLT and BLT combinations considered. We obtain a maximum efficiency of the tandem cell of η_{max}=14.1% for B_{gap}^{front}=1.9 eV, B_{gap}^{back} =1.5 eV, FLT=150 nm, and BLT=90 nm. These numbers are comparable to the predictions made by Dennler *et al.*[13] and Ameri *et al.*,[22] with similar band gaps for the front and back subcells. A comparison with the single cell case (11.7%) shows a maximum efficiency increase of 20%, which is a significant improvement, but it is far less than a doubling of the efficiency. As the subcell with the narrowest band gap has a broader absorption spectrum it is more profitable to situate the narrower band gap subcell in the back of the tandem cell. The reverse situation, represented by the local maximum of η=13.1% in Fig. 4 at B_{gap}^{front}=1.4 eV, B_{gap}^{back}=1.9 eV, FLT=40 nm, and BLT=200 nm, shows that the overlap of the absorption spectra leads to a reduction of the photon influx into the back subcell, leading to a decrease of the optimum FLT for the narrower band gap subcell and an increase of BLT for the wider band gap subcell. It should

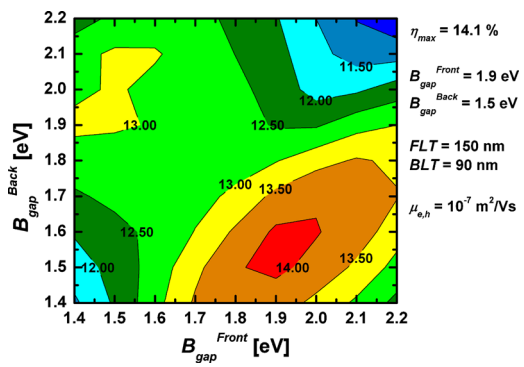

FIG. 4. (Color online) Power conversion efficiency η as a function of front layer polymer band gap B_{gap}^{front} and back layer polymer band gap B_{gap}^{back}. Note that 81 efficiencies in the plot are maximized with respect to FLT and BLT.

be noted that the η_{max} calculated here assumed [60]PCBM as the electron acceptor. The recent efficiency records reported for polymer:fullerene solar cells[8] all used [70]PCBM as an acceptor, in combination with a low band gap polymer. Since [70]PCBM absorbs in the visible, the absorption spectrum of the solar cell is broadened, leading to more absorption and higher efficiencies. This spectral broadening, however, makes it more difficult to exploit these cells in tandem structures since the second subcell will need to be shifted more to the infrared in order to be complementary with the broadened spectrum of the present low band gap record cells. So far, efficient solar cells based on these (near) infrared materials are not yet available, but when present they will open a route toward tandems that are able to exceed 14% efficiency.

In conclusion, the ultimate efficiency of organic tandem solar cells has been calculated using a combined optical and electrical device model. With this model the efficiencies of single cells have been evaluated as a reference, leading to a maximum efficiency of 11.7%. For tandem structures using a ZnO/PEDOT:PSS middle electrode an ultimate efficiency of 14.1% has been calculated. As a result tandem structures are expected to give a performance improvement of about 20% as compared to single cells.

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